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Structure and Stability of M−H_2 Complexes

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The potential stability of van der Waals complexes M−H_2 (M = Li, Be, B, C, Na, Mg, Al, Si) is assessed using quadratic configuration interaction and large basis sets. It is found that the alkali metals and alkaline earths form very weak complexes in their ground states, but much stronger complexes in their (p) excited states. The elements B, Al, C, and Si form both linear ($C_{\infty v}$) and perpendicular (C_{2v}) complexes, with greater thermodynamic stability in the latter arrangements. The complexes formed by C are likely to be kinetically unstable, and the same may be the case for Si. On the other hand, the complexes formed by B and Al are predicted to be quite stable.

Introduction

The structure and energetics of van der Waals complexes between metal atoms and molecular hydrogen are of considerable current theoretical and practical interest. There is, for example, currently considerable interest[1] in doping solid hydrogen with a small amount (<5%) of light metal atoms, since many of the lighter metals react more exothermally with oxygen than does hydrogen. The key is to determine if these metals can form weakly bound (e.g., van der Waals) species, so that oxidation does not have to overcome the binding energy of stronger M−H bonds (presumably, the amount of metal present would be small enough that M−M bonds would not be a consideration). This means that if a van der Waals species exists, to be useful it must be separated from any lower energy hydride by a substantial barrier, and there must not be an intersystem crossing that effectively lowers or even destroys the barrier.

In addition to the foregoing, it is also of interest from a purely academic perspective to understand the nature and the strength of weak metal−hydrogen interactions. Because these interactions are so weak, such predictions are challenging and require highly correlated wave functions with extended basis sets.

The most interesting metals M, based on the heats of formation of their corresponding oxides, appear to be Li, Be, B, C, Na, Mg, Al, and Si. Therefore, in this work we have carried out a preliminary study of the potential energy surfaces that connect the separated species M + H_2, potential van der Waals species, and the much more stable hydrides, in order to determine barrier heights on the adiabatic surfaces and to identify state crossings that might lead to unwanted nonadiabatic couplings. In addition, the binding energies for the van der Waals complexes are estimated.

The Li-H_2 system has been of particular interest because of the low mass of Li. Both the ground and excited states have been studied previously.[2−7] Hobza and Schleyer[3] studied Li−H_2 at the MP2/6-311G (2d,2p) level of theory and found a weakly bound complex (~7 cm^{-1} binding energy) for the ground state linear configuration and a much stronger complex (16.4 kcal/mol) for the excited state ($^2B_2$). Konowalow found the linear van der Waals complex to have a dissociation energy (D_e) between 13 and 18 cm^{-1} using the interacting correlated fragments (ICF) method and large basis sets.[5] Potential energy surfaces of Li−H_2 ground and lowest excited electronic states, including crossing regions, have been studied with MCSCF wave functions and rather small basis states (4-31G*).[6−7] A minimum with D_e about 10 kcal/mol was found on the $^2B_2$ surface, and the transition from $^2B_2$ to $^2A_1$ was predicted to occur with high probability. Potential energy surfaces have also been studied for Na−H_2,[8−10] Be−H_2,[11−13] and Mg−H_2[13−15] excited states. Augspurger and Dykstra found van der Waals complexes for Mg−H_2 and Mg−HF ground states using the coupled cluster method and triple-zeta quality basis sets.[16] The B−H_2 potential surface has been studied extensively by Alexander,[17] who found the B−H_2 complex to be stable kinetically. On the contrary, a practically negligible barrier was found for the C + H_2 reaction.[18−20]

In this paper we report preliminary results for M−H_2 complexes with M = Li, Be, B, C, Na, Mg, Al, and Si in their ground and some excited states, in order to determine the nature of their potential energy surfaces. This will provide some insight regarding the thermodynamic and kinetic stability of these species. The potential energy surfaces of those compounds found to be kinetically stable will be examined later in more detail.

Method of Calculation

The calculations were carried out using the quadratic configuration interaction method QCISD(T).[21] Fourth-order perturbation theory (MP4SDQ)[22] was used for some large complexes that contain 3−4 H_2 molecules. The basis sets used were correlation consistent valence-triple-zeta (cc-pVTZ)[23] for Li, Be, Na, and Mg and augmented aug-cc-pVTZ[24−26] for the other metal atoms and hydrogen.

This computational method was tested for Li- - -H_2 and B- - -H_2 complexes, since these species have been calculated previously using multireference configuration interaction (MRCI) methods and large basis sets.[5,17] The comparison of our QCISD(T) and MP4SDQ results with those of Konowalow for LiH_2[5] and Alexander for BH_2[17] are presented in Table 1. For the equilibrium geometry of the B- - -H_2 complex, found by Alexander[17] (R_{B-H_2} = 3.11 Å, r_{H-H} = 0.742 Å), the dissociation energy is 128 cm^{-1} at the QCISD(T)/aug-cc-pVTZ level of theory as compared with 121 cm^{-1} obtained with MRCI(D)/aug-cc-pVTZ.[17] Dissociation energies for Li- -H_2 complexes are also in a good agreement with ref 5: 15 vs 17 cm^{-1} for the linear complex and 9 vs 11 cm^{-1} for the perpendicular one. (The perpendicular structure, however, is found to be a transition state on the potential energy surface of Li−H_2 at the QCISD-

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TABLE 1: Comparison of Different Methods and Basis Sets

M	state	R(M−X),[a] Å	D_e, cm^{-1}	method
Li	$^2\Sigma$	5.2	13	MP4SDQ/aug-cc-pVTZ
		5.2	13	QCISD/aug-cc-pVTZ
		5.2	15	QCISD(T)/aug-cc-pVTZ
		5.1	17	ICF-CI/CASSCF[b]
B	$^2B_2$	3.1	121	MR-CI(D)/aug-cc-pVTZ[c]
			115	MP4SDQ/aug-cc-pVDZ
			98	QCISD/aug-cc-pVDZ
			119	QCISD(T)/aug-cc-pVDZ
			121	MP4SDQ/aug-cc-pVTZ
			102	QCISD/aug-cc-pVTZ
			128	QCISD(T)/aug-cc-pVTZ
			116	MP4SDQ/cc-pVTZ[d]
			100	QCISD/cc-pVTZ
			127	QCISD(T)/cc-pVTZ
			119	MP4SDQ/cc-pVQZ[d]
			101	QCISD/cc-pVQZ
			130	QCISD(T)/cc-pVQZ
A1	$^2B_2$	3.22	152	QCISD(T)/aug-cc-pVDZ
			204	QCISD(T)/aug-cc-pVTZ
			210	QCISD(T)/aug-cc-pVQZ

[a] X = midpoint of H−H bond. r(H−H) = 0.742 Å. [b] Reference 5. [c] Reference 17. [d] Augmented basis set on H atoms.

(T) level of theory). It is also seen from Table 1 that MP4SDQ consistently reproduces QCISD(T) results, while QCISD significantly underestimates binding.

The results obtained using different basis sets from pVDZ to pVQZ are shown in Table 1 for B and Al complexes. In general, pVDZ is not an adequate basis set for such calculations, but pVTZ and pVQZ yield very similar results. We used the pVTZ-type of basis set for the rest of our calculations, assuming that it is nearly converged. It was shown previously[27−31] that the augmented correlation consistent pVTZ basis set is converged with respect to basis set superposition errors.

All of the calculations described here were performed using the Gaussian-92 program.[32] Since QCISD(T) analytic gradients are not available, the potential energy surfaces for M−H_2 van der Waals complexes were studied by calculating grids of single-point energies at different values of M−H_2 and H−H distances. The calculations described in this paper were performed at linear ($C_{\infty v}$) and perpendicular (C_{2v}) geometries only. The structures found to be minima on the potential energy surfaces with restricted symmetry were verified to be minima or transition states by calculating numerical Hessians. The potential energy curves shown in all figures of this paper were obtained as follows: the M−H_2 distances were fixed at different values and the H−H distances were optimized for each M−H_2 distance; that is, R(M−H_2) was used as an approximation to a reaction coordinate. Note that the points that appear to be crossing points on these pictures do not correspond to real crossings, since the two states have the same R(M−H_2) distance, but different r(H−H) distances, optimal for each state. The curves shown should not be considered as reaction paths, since R(M−H_2) is not always a valid approximation to a reaction coordinate. These curves serve only as an approximate way to show part of the potential surfaces of M−H_2 systems and to give some idea about kinetic stabilities of van der Waals complexes. Positions of minimum energy crossing points between different states are discussed in the following section.

Results and Discussion

The calculated geometries of van der Waals complexes and their dissociation energies are shown in Table 2.

1. Complexes of s-Elements. According to our calculations, s-elements in their ground states (^{2}S, Li, Na and ^{1}S, Be, Mg) form only linear complexes with H_2. The dissociation energies are very small for these complexes. They are similar for Li and Na (about 15 cm^{-1}) and for Be and Mg (about 30 cm^{-1}). The Be and Mg complex energy wells are twice as deep as those for Li and Na and have M−H_2 distances that are shorter by about 1 Å (see Table 2). There are also local minima within C_{2v} symmetry, but they are not stable to bending (breaking C_{2v} symmetry). It is concluded that the C_{2v} complexes correspond to transition states between linear configurations at the level of theory used here. The barrier heights corresponding to these rotations are 6 and 5 cm^{-1} for Li and Na and 13 and 12 cm^{-1} for Be and Mg complexes.

On the other hand, C_{2v} complexes correspond to minima and are very stable (Table 3) for excited states of these elements (^{2}P Li,Na and ^{3}P Be,Mg) due to interactions of occupied p-orbitals with σ^*(H−H). The dissociation energies for $^2B_2$ complexes of Li and Na are 18 and 9 kcal/mol; for $^3B_2$ complexes of Be and Mg the dissociation energies are 20 and 6 kcal/mol at the QCISD(T) level of theory and basis sets used here. However, as shown in Figures 1 and 2, these complexes may be unstable kinetically due to crossings with ground state A_1 surfaces. These crossings suggest that sufficiently strong nonadiabatic coupling between the states could result in predissociation of the excited state complexes.

We have also done calculations on Be$(H_2)_n$ complexes with $n = 2-4$ and found their dissociation energies to change almost additively with the number of H_2 molecules: 33, 65, 99, and 132 cm^{-1} for $n = 1$, 2, 3, and 4, respectively (see Figure 3). Of course, this additivity is likely to be related to symmetry. If species having lower symmetry exist, the binding may vary somewhat for each additional H_2.

2. Complexes of B and Al. As noted above, the MRCI B−H_2 potential energy surface has been studied by Alexander.[17] He found the B-H_2 van der Waals complex to be stable to insertion of B into H_2. The most stable complex (with D_e = 121 cm^{-1}) was found for a perpendicular orientation of the H_2 molecule, with a p-orbital of B parallel to the H−H bond ($^2B_2$

TABLE 2: Characteristics of QCISD(T) van der Waals Complexes of M Atoms with H_2 Molecule

M	state	R(M−X),[a] Å	D_e,[b] cm^{-1}	M	state	R(M−X), Å	D_e, cm^{-1}
Li	$^2\Sigma$	5.21	15	Na	$^2\Sigma$	5.50	13
	$^2A_1$[c]	5.40	9		$^2A_1$[c]	5.70	8
Be	$^1\Sigma$	4.21	33	Mg	$^1\Sigma$	4.66	30
	$^1A_1$[c]	4.35	20		$^1A_1$[c]	4.80	18
B	$^2\Sigma$	3.87	93	A1	$^2\Sigma$	4.62	89
	$^2B_2$	3.11	130		$^2B_2$	3.25	204
	$^2B_1$	3.33	78		$^2B_1$	3.60	103
C	$^1\Sigma$	3.61	120	Si	$^1\Sigma$	4.25	112
	$^3\Pi$	3.54	81		$^3\Pi$	4.15	84
	$^3A_2$	2.21[d]	324		$^3A_2$	2.25[d]	720

[a] X = midpoint of H−H bond. [b] With respect to dissociation to M (ground state) + H_2. [c] Transition states between two linear minima. [d] Equilibrium distance r(H−H) = 0.75 and 0.76 Å for C−H_2 and Si−H_2 $^3A_2$ complexes, and 0.743 Å for other complexes.

TABLE 3: Complexes of Li, Na, Be, and Mg Excited States with H_2 Molecule

M	state	R(M−X)[a], Å	R(H−H), Å	D_e[b]
Li	$^2B_2$	1.66	0.84	18.2 kcal/mol
	$^2B_1$	1.89	0.75	7.3 kcal/mol
	$^2\Sigma$	6.27	0.743	27 cm^{-1}
Na	$^2B_2$	2.14	0.79	9.2 kcal/mol
	$^2B_1$	2.36	0.75	3.8 kcal/mol
	$^2\Sigma$	7.27	0.743	19 cm^{-1}
Be	$^3B_2$	1.36	0.98	20.4 kcal/mol
	$^3B_1$	1.78	0.76	1.9 kcal/mol
	$^3\Sigma$	4.32	0.743	98 cm^{-1}
Mg	$^3B_2$	2.01	0.80	5.6 kcal/mol
	$^3B_1$	2.77	0.743	0.7 kcal/mol
	$^3\Sigma$	5.07	0.743	84 cm^{-1}

[a] X = midpoint of H−H bond. [b] With respect to Li, Na (^{2}P) + H_2 or Be, Mg(^{3}P) + H_2.

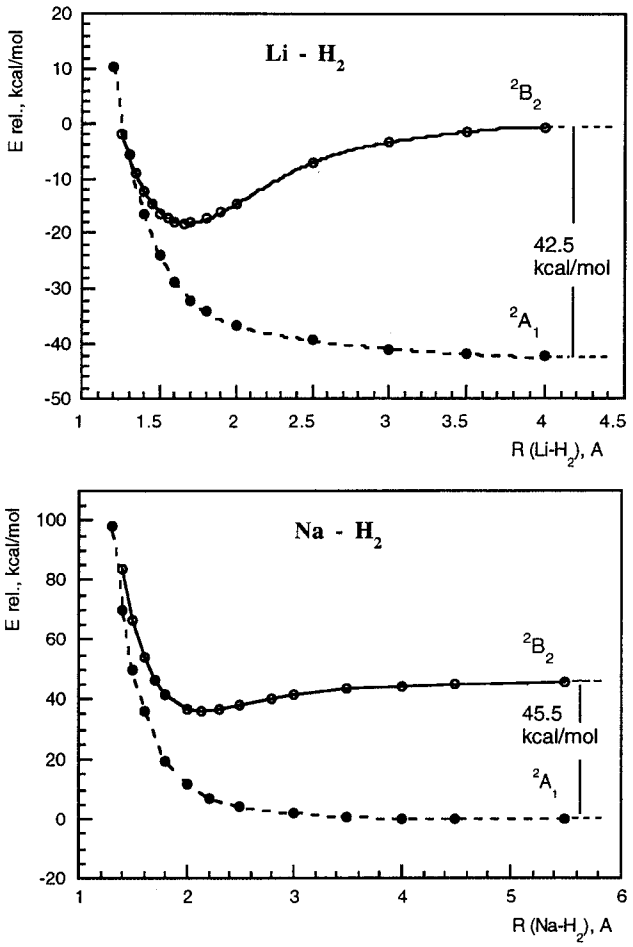

Figure 1. C_{2v} potential energy curves for Li−H_2 and Na−H_2 systems (QCISD(T)/aug-pvtz).

state). Less stable complexes were found on the $^2B_1$ (75 cm^{-1}) and $^2\Sigma$(68 cm^{-1}) potential energy surfaces. We have recomputed these complexes at the QCISD(T)/aug-pVTZ level to compare them with other complexes (Table 2). The agreement between QCISD(T) and MRCI is excellent for the $^2B_2$ and $^2B_1$ states, but QCISD(T) predicts a D_e of 93 cm^{-1} for the $^2\Sigma$ state, 25 cm^{-1} larger than that predicted by MRCI.

Three complexes were also found for the Al−H_2 system: linear $^2\Sigma$, and perpendicular $^2B_2$ and $^2B_1$. As in the case of the boron complexes, the most stable Al−H_2 complex is found for the $^2B_2$ state (D_e = 204 cm^{-1}).

The C_{2v} parts of the B−H_2 and Al−H_2 potential energy surfaces are shown in Figures 4 and 5. The minimum energy crossing between the $^2B_2$ (complex) and $^2A_1$ (ground) states of

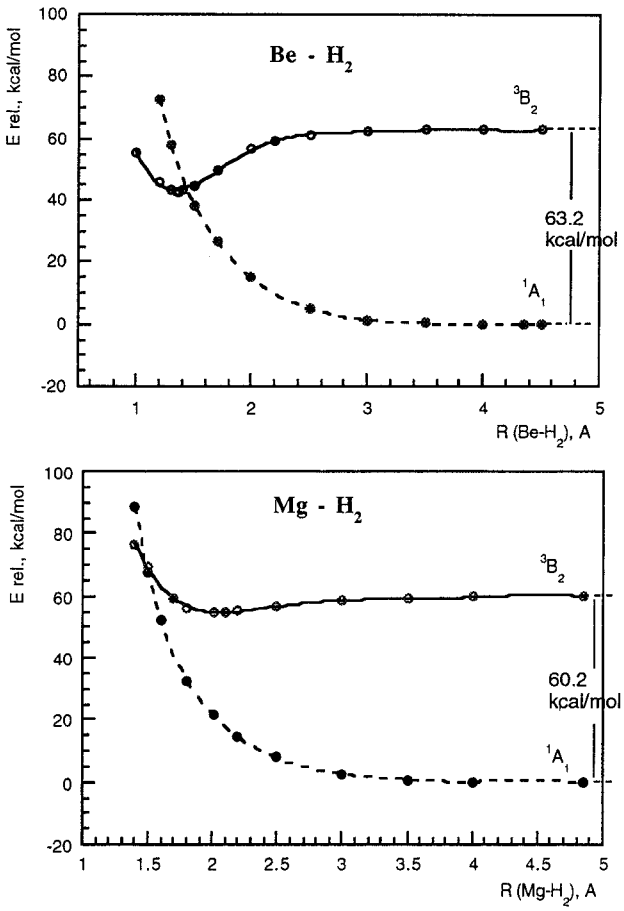

Figure 2. C_{2v} potential energy curves for Be−H_2 and Mg−H_2 systems (QCISD(T)/aug-pvtz).

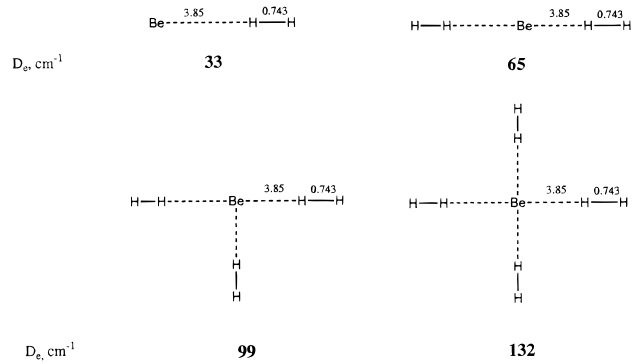

Figure 3. van der Waals complexes of Be with H_2 molecules (QCISD-(T)/aug-cc-pVTZ).

B−H_2 and Al−H_2, respectively, occurs in a region about 15 and 30 kcal/mol above the dissociation products B + H_2 and Al + H_2 at our level of theory. The geometries of these points (not shown in figure) are follows. B−H_2: R(B−H_2) = 1.25 Å, r(H−H) = 1.30 Å; Al−H_2: R(Al−H_2) = 1.50 Å, r(H−H) = 1.66 Å. The actual barriers for these reactions may occur in C_s symmetry. Then, they could correspond to avoided crossings and may be lower than the C_{2v} crossing points. The Al−H_2 potential energy surface, especially in the region of the crossing, will be analyzed in greater detail in the future using multiconfigurational wave functions. However, it is clear that the barrier to insertion of Al into H_2 is sufficient for the complex to be kinetically stable. The transition state on the $^2A_1$ surface, which separates the $^2A_1$ complex and the AlH_2 compound, is much higher in energy than the position of $^2B_2$−$^2A_1$ crossing (about 76 kcal/mol above Al + H_2), since the complex and the hydride

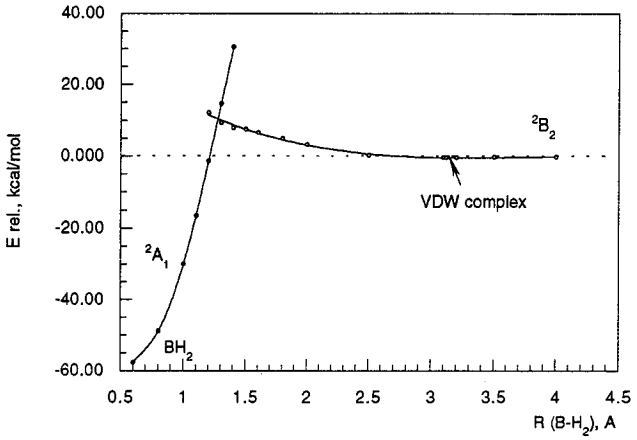

Figure 4. QCISD(T)/aug-pvtz potential energy surfaces for $B-H_2$ (C_{2v} symmetry).

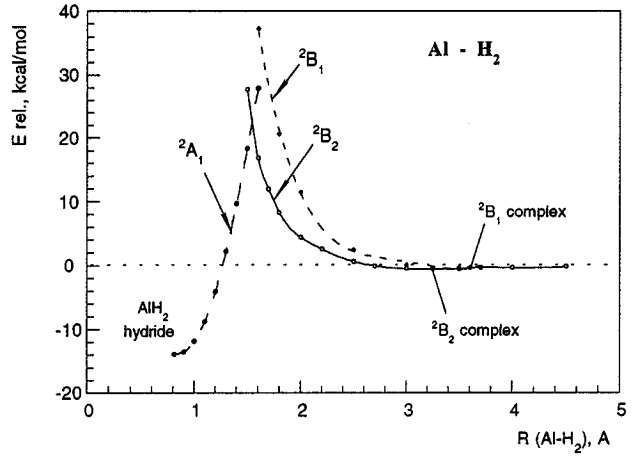

Figure 5. QCISD(T)/aug-pvtz potential energy surfaces for $Al-H_2$ (C_{2v} symmetry).

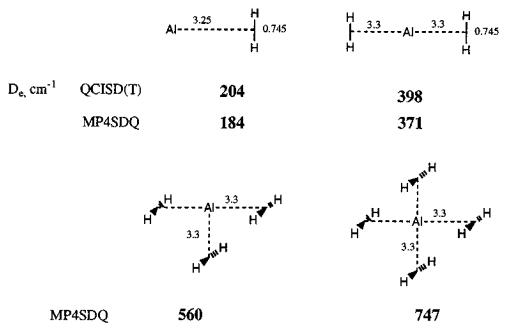

Figure 6. van der Waals complexes of Al and H_2 molecules.

have different electronic configurations. In the case of BH_2 Alexander has found this barrier to be about 55 kcal/mol. For both B and Al the insertion into the H−H bond is more likely to occur through the $^2B_2-^2A_1$ crossing rather than via the very high $^2A_1$ transition state.

The structures and stabilization energies for several $Al-(H_2)_n$ complexes with $n = 1-4$ are shown in Figure 6. Again, the addition of H_2 molecules increases the stability of the complex in an almost additive manner.

3. Complexes of C and Si. $C(^3P) + H_2$ potential energy surfaces were studied previously[18−20] at the CI level of theory with basis sets varying from minimal[18] to DZ.[19−20] It was found that within C_{2v} symmetry the $^3A_2$ state has a minimum corresponding to a van der Waals complex and that the $^3B_1$ state (corresponding to the CH_2 ground state) crosses $^3A_2$ about 2.5 kcal/mol above the dissociation to $C(^3P) + H_2$. The energy

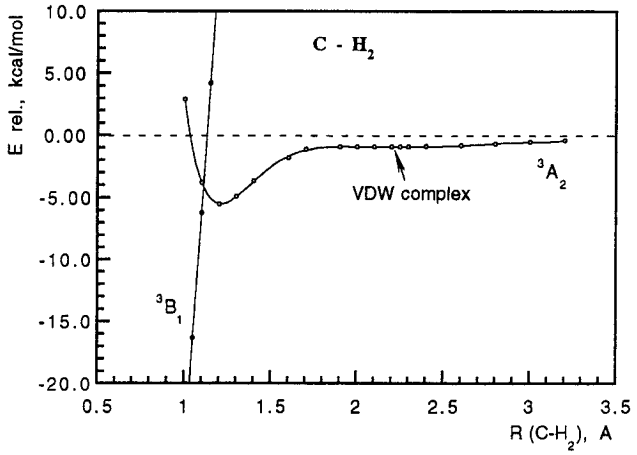

Figure 7. QCISD(T)/aug-pvtz potential energy surface for $C-H_2$ (C_{2v} symmetry).

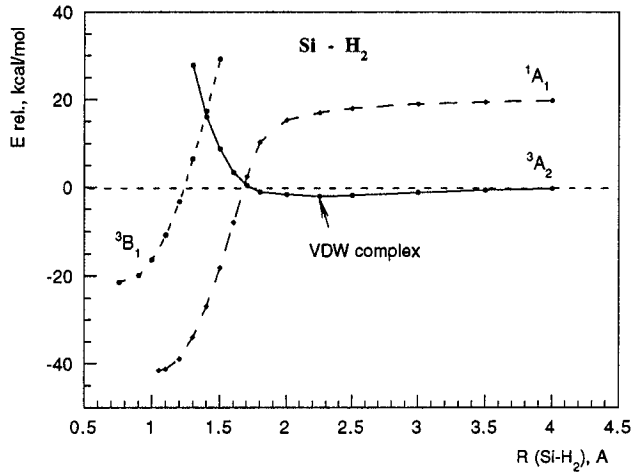

Figure 8. QCISD(T)/aug-pvtz potential energy surfaces for $Si-H_2$ (C_{2v} symmetry).

of the crossing point depends very much on the basis set: it decreases from 50 kcal/mol for a minimal basis set to 2.5 kcal/mol for the largest DZ basis set used in ref 20. It was found by Harding[20] that relaxation of C_{2v} symmetry to C_s leads to a very slight decrease in energy (about 1 kcal/mol) in the region of the crossing. We recalculated the C_{2v} part of the surface using QCISD(T) with the aug-pVTZ basis set and estimate that the $^3A_2$ and $^3B_1$ minimum energy crossing point (not shown in figure) occurs at 1.5 kcal/mol above the $C(^3P) + H_2$ dissociation energy. The $R(C-H_2)$ distance corresponding to the crossing point is 1.1 Å, and $r(H-H)$ is 1.28 Å. At this level of theory, the $^3A_2$ surface has a minimum corresponding to a weak van der Waals complex (with $D_e = 324$ cm^{-1}, $R = 2.2$ Å, $r = 0.75$ Å). Then, as $R(C-H_2)$ decreases, the $^3A_2$ potential curve after a very small barrier (10 cm^{-1}) goes down again and has another minimum with $R = 1.2$ Å, $r = 0.9$ Å and a dissociation energy about 5.5 kcal/mol (see Figure 7). This region obviously has to be studied with multiconfigurational wave functions, but it does not appear that there is a kinetically stable complex in the case of C.

While the $C + H_2 \rightarrow CH_2$ reaction goes practically without a barrier, the $Si(^3P) + H_2$ surface seems to be more promising (Figure 8). There is a $Si-H_2$ van der Waals complex on the $^3A_2$ surface which is 2 kcal/mol (720 cm^{-1}) deep, the $^3A_2$ and $^3B_1$ states crossing in a region that is 20 kcal/mol above the $Si-H_2$ complex. The approximate geometry of the minimum energy crossing point is $R(Si-H_2) = 1.4$ Å, $r(H-H) = 1.67$ Å. However, the $^1A_1$ state crosses $^3A_2$ at about 5 kcal above the

complex ($R(Si-H_2) = 1.6$ Å, $r(H-H) = 0.94$ Å), so these regions of the $Si-H_2$ potential energy surfaces must be explored in greater detail using multireference wave functions in order to evaluate the nonadiabatic interactions. No complex is found on the $^1A_1$ surface for either $C-H_2$ or $Si-H_2$: the insertion of singlet C and Si to H_2 goes with no barrier at all.

We have also considered the $C_{\infty v}$ approach for both triplet and singlet C and Si. Singlet ($^1\Sigma$) and triplet ($^3\Pi$) complexes with occupied p-orbitals along the molecular axis are found for linear configurations of $C-H_2$ and $Si-H_2$. Complexes found for $^1\Delta$ and $^3\Sigma$ states with occupied p-orbitals perpendicular to the molecular axis do not correspond to minima (unstable to bending). Linear complexes are much weaker than perpendicular ones (see Table 2 for dissociation energies and geometries of different complexes).

Conclusions

QCISD(T)/cc-pVTZ calculations have been performed for a series of van der Waals complexes $M-H_2$, where M = Li−C and Na−Si. We find that s-elements in their ground states form very weak linear complexes with dissociation energies of about 15 cm^{-1} (Li, Na) and 30 cm^{-1} (Be, Mg). p-Elements in their ground states form much stronger complexes due to interactions of the occupied p-orbital with the H_2 molecule. p-Elements form complexes with both linear and perpendicular geometries. Perpendicular complexes with the occupied p-orbital parallel to the H−H bond, however, are more stable thermodynamically, and their stability increases from B, Al to C, Si. The thermodynamic stability of perpendicular complexes increases from first- to second-row elements, while the stability of linear complexes remains almost the same. The equilibrium distance M−X (X-midpoint of H−H bond) of complexes decreases upon going from left to right across the periodic table and is very similar for elements of the same group.

Kinetic stability was studied for C_{2v} complexes, since thermodynamically stable MH_2 compounds with this symmetry exist for M = B, Al, C, Si. Complexes are kinetically stable only if barriers to insertion are high enough. van der Waals complexes and MH_2 compounds have different electronic states, and the energy of their crossing is the upper limit for the barrier of the reaction, which might occur due to an avoided crossing. B-H_2 and Al-H_2 ($^2B_2$) complexes are found to be kinetically stable. The minimum energy crossing point between $^2B_2$ and $^2A_1$ is estimated to be about 16 and 30 kcal/mol above the corresponding B and Al $^2B_2$ complexes. Complexes of C and Si are probably unstable kinetically (see Figures 7 and 8), although in the case of Si this depends on how strong is the interaction between triplet and singlet states near the crossing region. The regions of these potential surfaces close to surface crossings will be studied more carefully in a later work using multireference wave functions.

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References and Notes

(1) (a) Fajardo, M. E. *J. Chem. Phys.* **1993**, *98*, 110. (b) Fajardo, M. E.; Tam, S.; Thompson, T. L.; Cordonnier, M. E. *Chem. Phys.* **1994**, *189*, 351.
(2) Wagner, A. F.; Wahl, A. C.; Karo, A. M.; Krejci, R. *J. Chem. Phys.* **1978**, *69*, 3756.
(3) Hobza, P.; von R. Schleyer, P. *Chem. Phys. Lett.* **1984**, *105*, 830.
(4) García-Prieto, J.; Feng, W. L.; Novaro, O. *Chem. Phys. Lett.* **1985**, *119*, 128.
(5) Konowalow, D. Private communication. 1991.
(6) Toyama, M.; Uchide, T.; Yasuda, T.; Kasai, T.; Matsumoto, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2781.
(7) Matsumoto, S.; Mizutani, K.; Sekiguchi, A.; Yano, T.; Toyama, M. *Int. J. Quantum Chem.* **1986**, *XXIX*, 689.
(8) Botschwina, P.; Meyer, W.; Hertel, I. V.; Reiland, W. *J. Chem. Phys.* **1981**, *75*, 5438.
(9) Yarkony, D. R. *J. Chem. Phys.* **1986**, *84*, 3206.
(10) Halvick, P.; Truhlar, D. G. *J. Chem. Phys.* **1992**, *96*, 2895.
(11) Poirier, R. A.; Peterson, M. R.; Menzinger, M. *J. Chem. Phys.* **1983**, *78*, 4592.
(12) Kellö, V.; Sadlej, A. J. *Theor. Chim. Acta* **1992**, *81*, 417.
(13) Blickensderfer, R. P.; Jordan, K. D.; Adams, N.; Breckenridge, W. H. *J. Phys. Chem.* **1982**, *86*, 1930.
(14) Adams, N.; Breckenridge, W. H.; Simons, J. *Chem. Phys.* **1981**, *56*, 327.
(15) Rosenkrantz, M. E. *Proc. High Energy Density Matter Conf. April 1992*, Lancaster, CA **1992**.
(16) Augspurger, J. D.; Dykstra, C. E. *Chem. Phys. Lett.* **1989**, *158*, 399.
(17) Alexander, M. H. *J. Chem. Phys.* **1993**, *99*, 6014.
(18) Blint, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1975**, *32*, 178.
(19) Casida, M. E.; Chen, M. M. L.; MacGregor, R. D.; Schaefer III, H. F. *Isr. J. Chem.* **1980**, *19*, 127.
(20) Harding, L. B. *J. Phys. Chem.* **1983**, *87*, 441.
(21) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Phys. Chem.* **1987**, *87*, 5968.
(22) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.
(23) Woon, D. E.; Dunning, T. H. Jr., To be published.
(24) Dunning, Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
(25) Kendall, R. A.; Dunning, Jr., T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
(26) Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1993**, *98*, 1358.
(27) Feller, D. *J. Chem. Phys.* **1994**, *100*, 4981.
(28) Xantheas, S. S. *J. Chem. Phys.* **1993**, *99*, 8774.
(29) Del Bene, J. E. *Int. J. Quantum Chem. Sym.* **1992**, *26*, 527.
(30) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.
(31) Woon, D. E. *J. Chem. Phys.* **1994**, *100*, 2838.
(32) *Gaussian 92, revision C*; Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1992.

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